



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| <b>(51) International Patent Classification <sup>5</sup> :</b><br><b>C08F 297/04, C08G 81/02</b><br><b>C09J 153/02, 7/02</b>  | <b>A1</b> | <b>(11) International Publication Number:</b> <b>WO 92/20725</b><br><b>(43) International Publication Date:</b> 26 November 1992 (26.11.92)  |
| <b>(21) International Application Number:</b> PCT/US92/04334<br><b>(22) International Filing Date:</b> 22 May 1992 (22.05.92)<br><b>(30) Priority data:</b><br>705,193                      24 May 1991 (24.05.91)                      US<br><b>(71) Applicants:</b> THE DOW CHEMICAL COMPANY [US/<br>US]; 2030 Dow Center Abbott Road, Midland, MI 48640<br>(US). EXXON CHEMICAL PATENTS INC. [US/US];<br>5200 Bayway Drive, Baytown, TX 77522 (US).<br><b>(72) Inventors:</b> DIEHL, Charles, F. ; 4828 Front Royal Drive,<br>Baton Rouge, LA 70817 (US). MARCHAND, Gary, R. ;<br>4028 Lassen Drive, Baton Rouge, LA 70814 (US). MY-<br>ERS, Michael, O. ; 16716 Bristoe Avenue, Baton Rouge,<br>LA 70816 (US). TANCREDE, Jean, M. ; 936 Shady-<br>brook Drive, Baton Rouge, LA 70816 (US).  |           | <b>(74) Agents:</b> HEWITT, Lester, L. et al.; Pravel, Gambrell, He-<br>witt, Kimball & Krieger, 1177 West Loop South, 10th<br>Floor, Houston, TX 77027-9095 (US).<br><b>(81) Designated States:</b> AT (European patent), AU, BB, BE<br>(European patent), BF (OAPI patent), BG, BJ (OAPI<br>patent), BR, CA, CF (OAPI patent), CG (OAPI patent),<br>CH (European patent), CI (OAPI patent), CM (OAPI<br>patent), CS, DE (European patent), DK (European pa-<br>tent), ES (European patent), FI, FR (European patent),<br>GA (OAPI patent), GB (European patent), GN (OAPI<br>patent), GR (European patent), HU, IT (European pa-<br>tent), JP, KP, KR, LK, LU (European patent), MC (Eu-<br>ropean patent), MG, ML (OAPI patent), MN, MR (OA-<br>PI patent), MW, NL (European patent), NO, PL, RO,<br>RU, SD, SE (European patent), SN (OAPI patent), TD<br>(OAPI patent), TG (OAPI patent).<br><br><b>Published</b><br><i>With international search report.</i> |
| <b>(54) Title:</b> RADIAL BLOCK COPOLYMERS, HOT MELT ADHESIVE COMPOSITIONS, AND ARTICLES PRODUCED THEREFROM<br><br><b>(57) Abstract</b><br><p>Radial block copolymers characterized by the formulae: (1) (pS-pI)<sub>n</sub>X and (2) (pS-pI-pB)<sub>n</sub>X where pS is polystyrene, pI is polyisoprene, pB is butadiene, X is a residue of a multifunctional coupling agent used in the production of the radial block copolymer, and n is a number greater than 2 representative of the number of branches appended to X; hot-melt adhesive compositions constituted of said radial block copolymers, and articles of manufacture produced therefrom. These copolymers possess blocks of high average molecular weight polystyrene (10,000 to 25,000) and an overall average molecular weight (90,000 to 380,000) such that when blended in requisite proportions with a compatible tackifier resin, preferably also a secondary tackifying resin or plasticizing oil, and stabilizer, superior hot-melt adhesive compositions can be formed. The hot-melt adhesive compositions possess, inter alia, superior heat resistance, superior static time to failure with low viscosity, good peel adhesion, good tack, and high ability to bond to a polyethylene or polypropylene substrate at temperatures below that which may damage the substrate.</p> |           |  |

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RADIAL BLOCK COPOLYMERS, HOT MELT ADHESIVES  
COMPOSITIONS, AND ARTICLES PRODUCED THEREFROM

1                   1.   Field of the Invention

2                   This invention relates to radial block  
3 copolymers, hot-melt adhesive compositions, and  
4 articles formed or constructed therefrom. In parti-  
5 cular, it relates to radial block copolymers consti-  
6 tuted of resinous polystyrene block segments and  
7 resinous polydiene block segments, specifically a  
8 polyisoprene block or a predominantly polyisoprene  
9 block containing polybutadiene, and to improved hot-  
10 melt adhesive compositions formed from said block  
11 copolymers, especially adhesives of a type useful in  
12 the assembly of disposable articles, particularly  
13 disposable articles wherein the hot-melt adhesive  
14 composition is employed in the construction to bond a  
15 polyethylene or polypropylene substrate to a tissue,  
16 non-woven fabric or absorbent fluff.

17                   2.   Background

18                   It is known to prepare hot-melt adhesive  
19 compositions from polystyrene-polyisoprene-  
20 polystyrene and polystyrene-polybutadiene-polysty-  
21 rene block copolymers. Linear polystyrene-polyiso-  
22 prene-polystyrene block copolymers, hot melt adhesive  
23 compositions based on these block copolymers,  
24 articles produced from these adhesives, are disclosed  
25 in U.S. Patent Application Serial No. 393,545.

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1 supra. The linear polystyrene-polyisoprene-polysty-  
2 rene block copolymer; or linear, pS-pI-pS block  
3 copolymer, disclosed by this application is character-  
4 rized by any of the formulas: (1)  $\text{pI}-(\text{pS-pI})_n$ ,  
5 where n is 2, or greater than 2; (2)  $\text{pS}-(\text{pI-pS})_n$ ,  
6 where n is 1, or greater than 1; or (3)  $(\text{pS-pI})_n$ ,  
7 where n is 2, or greater than 2; wherein, in any of  
8 formulas (1), (2) or (3), pS is a polystyrene block  
9 having an average molecular weight ranging from about  
10 12,000 to about 20,000, preferably from about 14,000  
11 to about 19,000, pI is a polyisoprene block having an  
12 average molecular weight ranging from about 30,000 to  
13 about 70,000, preferably from about 35,000 to about  
14 60,000, the overall molecular weight of the block  
15 copolymer ranges from about 60,000 to about 110,000,  
16 preferably from about 70,000 to about 95,000, and the  
17 polystyrene block pS components are present in an  
18 amount of at least about 27 parts to about 50 parts,  
19 preferably from about 35 parts to about 45 parts, per  
20 100 parts by weight of the block copolymer. The  
21 pS-pI-pS block copolymer, in all embodiments is char-  
22 acterized by the presence of a pI block, or polyiso-  
23 prene block, located between two pS blocks, or  
24 polystyrene blocks which may or may not be terminal  
25 endblocks. The pS-pI-pS block copolymer can thus be  
26 either a triblock or multi-block copolymer, though  
27 the triblock copolymer is preferred.

28 The hot melt adhesive composition is con-  
29 stituted of the pS-pI-pS block copolymer, a compati-  
30 ble primary tackifier resin, preferably also a  
31 secondary tackifier or plasticizing resin or plasti-  
32 cizing oil, and stabilizer. These block copolymers,  
33 when blended in the requisite proportions with these  
34 components, produce adhesives with high shear holding  
35 power and shear adhesion failure temperature, and a

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1 low overall molecular weight sufficient to provide  
2 low viscosity. These adhesives have, inter alia,  
3 been found admirably suitable for the construction of  
4 disposable articles wherein the adhesive is applied  
5 as a continuous or discontinuous phase between  
6 members, e.g., via brushing, spraying or air-extru-  
7 sion, between members to be bound together, particu-  
8 larly disposable articles of multi-line construction  
9 wherein the adhesive is supplied as fine parallel  
10 longitudinal strips, or as a multi-dot pattern of  
11 adhesive droplets, to bond together a moisture  
12 impervious outer polyethylene or polypropylene sheet  
13 and an inner moisture adsorbent sheet, or tissue, as  
14 used in diaper constructions. They have also been  
15 found suitable for use in the construction of  
16 sanitary napkins, bed pads, and with or without the  
17 addition of other materials, are useful for packaging  
18 and carton sealing, magazine and book lining, or book  
19 binding, or as elastic glues generally.

21 Adhesives formed from this type of pS-pI-pS  
22 block copolymer has been found admirably suitable,  
23 e.g., in the production of "multi-line" (or multi-  
24 dot) constructions. Hot-melt adhesives applied in  
25 the form of fine parallel longitudinal strips (or as  
26 patterns of dots) have been found to possess suffi-  
27 cient adhesive and cohesive strength to provide high  
28 bond strength values so that when subjected to stress  
29 the constructions cannot be easily separated.  
30 Moreover, the adhesives can withstand high mixing and  
31 application temperatures without thermal degradation  
32 and loss of adhesive properties, and have good heat  
33 and oxidation resistance on aging. The adhesives  
34 also perform well at moderate temperatures, which is  
35 required since the disposable articles are worn at

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1 body temperature; and they also perform well at  
2 higher temperatures, which is also required since the  
3 constructed articles must also be exposed to elevated  
4 temperatures during warehousing and shipping.  
5 Furthermore, these hot-melt adhesives have low adhe-  
6 sive viscosity such that they can be applied at low  
7 temperature in order to avoid distortion of the  
8 polyethylene or polypropylene substrates to which the  
9 adhesive is applied. Nonetheless, there remains a  
10 need for hot-melt adhesives useful in magazine and  
11 book binding, elastic gluing operations generally,  
12 hot-melt adhesive compositions useful in the assembly  
13 of multi-line constructions, and disposable articles  
14 of multi-line construction formed from improved  
15 hot-melt adhesive compositions.

### 16 3. Objects

17 It is, accordingly, a primary objective of  
18 this invention to fulfill these and other needs.

19 A particular object of this invention is to  
20 provide novel radial block copolymers constituted of  
21 a polystyrene block segment and a polydiene block  
22 segment, viz. a polyisoprene block or a polyisoprene  
23 block containing some polybutadiene, and improved  
24 hot-melt adhesive compositions particularly useful in  
25 the assembly of disposable articles of manufacture,  
26 particularly disposable articles of multi-line  
27 construction, formed from such radial block copoly-  
28 mers.

29 A further, and more particular object is to  
30 provide hot-melt adhesive compositions which have  
31 superior heat resistance, superior static time to  
32 failure with low viscosity, good peel adhesion, and  
33 good tack and high ability to bond to a polyethylene  
34 or polypropylene substrate at temperature below that  
35 which would be injurious to the substrate.

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1           A further, and yet more specific object is  
2 to provide disposable articles as previously des-  
3 cribed, particularly disposable articles of multi-  
4 line or multi-dot construction, wherein a polyethy-  
5 lene or polypropylene substrate is bonded to a  
6 tissue, or non-woven polyethylene or polypropylene  
7 substrate, or both, via the use of said improved hot-  
8 melt adhesive compositions.

9           4.   The Invention

10           These objects and others are achieved pur-  
11 suant to the practice of this invention, embodying a  
12 novel radial block copolymer constituted of resinous  
13 polystyrene block segments and resinous polydiene  
14 block segments, suitably a polyisoprene block or a  
15 predominantly polyisoprene block containing a rela-  
16 tively small amount of polybutadiene, and a novel  
17 hot-melt adhesive composition comprising said novel  
18 copolymer, compatible primary tackifier resin,  
19 preferably also a secondary tackifier resin or  
20 plasticizing oil, and stabilizer. The hot-melt  
21 adhesive composition is, in particular, comprised of  
22 said radial block copolymers the polystyrene blocks  
23 of which are sufficiently high average molecular  
24 weight to provide, inter alia, when blended in the  
25 requisite proportions with a compatible tackifier  
26 resin, preferably also a secondary tackifier resin or  
27 plasticizing oil, and stabilizer, high shear holding  
28 power and shear adhesion failure temperature, and a  
29 low overall molecular weight sufficient to provide  
30 low viscosity.

31           The novel radial polystyrene-polyisoprene  
32 or polystyrene-polyisoprene/polybutadiene block  
33 copolymer is characterized by the formulas:

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1 (1)  $(pS-pI)_nX$

2 (2)  $(pS-pI-pB)_nX$

3 where pS is polystyrene, pI is polyisoprene, pB is  
4 polybutadiene, X is a residue of a multifunctional  
5 coupling agent used in the production of the radial  
6 block copolymer, and n is a number greater than 2,  
7 and representative of the number of branches appended  
8 to X. The number n, for  $(pS-pI)_nX$  block copolymers,  
9 will on the average range from above 2 to about  
10 6, preferably above about 3 to about 5; and for  
11  $(pS-pI-pB)_nX$  block copolymers, on the average will  
12 range from above about 3 to about 7, preferably above  
13 about 3.5 to about 4. In either formula (1) or (2),  
14 pS is a polystyrene block having an average number  
15 molecular weight ranging from about 10,000 to about  
16 25,000, preferably from about 14,000 to about 20,000,  
17 and pI is a polyisoprene block having an average  
18 number molecular weight ranging from about 20,000 to  
19 about 70,000, preferably from about 20,000 to about  
20 40,000. In formula (2), pI-pB is a polyisoprene/  
21 polybutadiene block, or polyisoprene block an end of  
22 which contains butadiene, or polybutadiene, and the  
23 pI-pB component is one having a total average number  
24 molecular weight ranging from about 20,000 to about  
25 70,000, preferably from about 20,000 to about  
26 40,000. The overall number average molecular weight  
27 of the radial block copolymer in accordance with  
28 either formula (1) or formula (2) ranges from about  
29 90,000 to about 380,000, preferably from about  
30 100,000 to about 240,000, more preferably  
31 from about 120,000 to about 200,000, and the polysty-  
32 rene block pS components are present in an amount of  
33 at least about 25 parts to about 50 parts, preferably  
34 from about 27 parts to about 45 parts, per 100 parts  
35 by weight of the radial block copolymer.



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1                   The radial block copolymers of this in-  
2 invention are thus constituted of resinous polysty-  
3 rene block segments and resinous polydiene block  
4 segments, suitably, in accordance with formula (1),  
5 of polyisoprene, pI; or, in accordance with formula  
6 (2), of polyisoprene and polybutadiene, pI-pB. Thus,  
7 styrene is employed to make the resinous pS block  
8 segments of both the  $(pS-pI)_nX$  and  $(pS-pI-pB)_nX$   
9 block copolymers. In accordance with formula (1),  
10 isoprene is employed to make the resinous pI block  
11 segments, the  $(pS-pI)$  polymer chains being formed by  
12 sequential polymerization of isoprene with the pS.  
13 The  $(pS-pI)$  polymer chains, suitably as pS-pI-Li  
14 living polymer chains, are coupled with coupling  
15 agents possessing at least three, and preferably four  
16 sites reactive toward carbon-lithium bonds, e.g.,  
17  $SiCl_4$ , to form the radial or multiblock  $(pS-pI)_nX$   
18 copolymer. In forming the radial or multiblock  
19 copolymer described by formula (2), i.e.,  
20  $(pS-pI-pB)_nX$ , pS-pI-pB-Li polymer chains are formed  
21 by the sequential polymerization of living pS-pI-Li  
22 polymer chains with butadiene. The radial or multi-  
23 block  $(pS-pI-pB)_nX$  copolymers are correspondingly  
24 made by coupling the pS-pI-pB-Li living polymer  
25 chains with the multi- or tetra functional coupling  
26 agent, e.g.,  $SiCl_4$ . Thus, the styrene is polymer-  
27 ized to form pS, the isoprene is then introduced to  
28 form pS-pI, the butadiene is then introduced to form  
29 pS-pI-pB, and the pS-pI-pB chains are then coupled  
30 with the tetrafunctional coupling agent to form the  
31  $(pS-pI-pB)_nX$  radial or multiblock polymer. In the  
32 pI-pB segment of the  $(pS-pI-pB)_nX$  polymer, the  
33 polyisoprene is present in amount sufficient to  
34 impart predominantly polyisoprene characteristics,  
35 not butadiene or polybutadiene characteristics, to

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1 the polymer. Thus, in the pI-pB segments of the  
2 polymer, the weight amount of polyisoprene will  
3 exceed 50 percent of the total weight of diene in the  
4 polymer, i.e.,  $pI/(pI + pB) > 50 \text{ wt.}\%$ . Conversely,  
5 the weight amount of butadiene or polybutadiene will  
6 be less than 50 percent of the total weight of diene  
7 in the polymer, i.e.,  $pB/(pI + pB) < 50 \text{ wt.}\%$ .  
8 Preferably the polybutadiene portion of the diene  
9 segment is less than 10 percent, most preferably less  
10 than 5 percent, based on the total weight of the  
11  $(pI + pB)$ , or diene component of the polymer.

12 The small amount of butadiene at the end of  
13 the diene midblock is useful in that it enhances the  
14 coupling reaction in formation of the polymer, and  
15 results in a radial polymer with a higher number of  
16 branches. A further description of the process at  
17 this point will facilitate an understanding of this  
18 feature of the invention. The radial polymers of  
19 this invention are thus synthesized by first contact-  
20 ing styrene polymer with an initiator, suitably e.g.,  
21 a sec-butyllithium initiator, in the presence of an  
22 inert diluent, e.g., cyclohexane. A living polymer  
23 is then formed, as represented e.g., by the simpli-  
24 fied structure pS-Li. The living polystyrene polymer  
25 pS-Li is next contacted with an isoprene monomer;  
26 the resulting product being represented by the  
27 simplified structure pS-pI-Li. The living polymer is  
28 then "coupled" by reacting the pS-pI-Li with a multi-  
29 functional coupling agent, or agent which has three  
30 or more sites, e.g.,  $SiCl_4$ , to produce a polymer with  
31 a radial or branched structure which may be represen-  
32 ted as  $(pS-pI)_nX$ , where X is a residual of the multi-  
33 functional coupling agent, and n is a number greater  
34 than 2. Alternately, the living polymer pS-pI-Li can  
35 be contacted with a small amount of butadiene monomer

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1 to produce a living polymer with the structure  
2 pS-pI-pB-Li, where pB represents butadiene or  
3 polybutadiene. Coupling of the pS-pI-pB-Li with the  
4 coupling agent produces a branched block copolymer  
5 with the structure  $(\text{pS-pI-pB})_n\text{X}$ . The radial polymer  
6 that is produced, using  $\text{SiCl}_4$  as a coupling agent,  
7 will on the average produce  $(\text{pS-pI-pB})_n\text{X}$  polymers  
8 where n approximates 4, whereas, in contrast, in  
9 producing  $(\text{pS-pI})_n\text{X}$  polymers in an otherwise similar  
10 manner it will be found that n will more closely  
11 approximate 3. The butadiene need be added only in  
12 amount necessary to assure that the ends of all of  
13 the pI segments of the polymer chains are provided  
14 with at least one molecule of butadiene, though as  
15 suggested the butadiene can be added in larger  
16 amounts. The radial block copolymers of this  
17 invention, in either event, have been found to pro-  
18 duce unexpectedly good hot melt adhesives when com-  
19 bined with suitable tackifier resins, plasticizer  
20 oils, and antioxidants.

21 Useful coupling agents are those possess-  
22 ing three or more, preferably four, sites reactive  
23 toward carbon-lithium bonds. Suitable coupling  
24 agents are those compositions of the formula  $\text{X(L)}_n$   
25 where X represents the coupling moiety residue,  
26 and L is a suitable leaving group. Exemplary of  
27 coupling agents of this type are silica halides,  
28 e.g.,  $\text{SiCl}_4$ , or a silane compound where one or more  
29 of the halides is substituted by a hydrocarbyl group,  
30 e.g., methyl trichlorosilane; epoxy compounds, e.g.,  
31 epoxidized linseed oil, epoxidized soybean oil;  
32 acrylate multi esters, e.g., pentaerythritol tetra-  
33 acrylate; epoxy silanes; divinyl compounds, e.g.,  
34 divinyl benzene, and the like.

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1           The hot-melt adhesive composition is, in  
2 particular, comprised of from about 15 percent to  
3 about 35 percent, preferably from about 20 percent to  
4 about 30 percent, based on the weight of the hot-melt  
6 adhesive composition, of said radial block copolymer  
7 wherein the pI component or pI-pB component, respect-  
8 tively, is one having an average molecular weight  
9 ranging from about 20,000 to about 70,000, preferably  
10 from about 20,000 to about 40,000, the pS component  
11 is polystyrene having an average molecular weight  
12 ranging from about 10,000 to about 25,000, preferably  
13 from about 14,000 to about 20,000, the overall  
14 molecular weight of the block copolymer ranges from  
15 about 90,000 to about 380,000, preferably from about  
16 100,000 to about 240,000, and wherein the pS compo-  
17 nent is present in an amount of at least about 25  
18 parts up to about 50 parts, preferably from about 27  
19 parts to about 45 parts, per 100 parts by weight of  
20 the radial block copolymer; from about 45 percent to  
21 about 70 percent, preferably from about 50 percent to  
22 about 60 percent, based on the weight of the hot-melt  
23 adhesive composition, of a compatible primary tacki-  
24 fying resin; from 0 percent to about 30 percent,  
25 preferably from about 5 percent to about 20 percent,  
26 of a plasticizing oil, or secondary tackifying resin,  
27 or both, based on the weight of the hot-melt adhesive  
28 composition; and from about 0.1 percent to about 2  
29 percent, preferably from about 0.5 percent to about  
30 1.5 percent of a stabilizer, based on the weight of  
31 the hot-melt adhesive composition.

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1                   These hot-melt adhesive compositions, con-  
2     stituted of a (pS-pI)<sub>n</sub> X or (pS-pI-pB) X radial block  
3     copolymer of intermediate to relatively high styrene  
4     content and overall low molecular weight to which the  
5     primary tackifying resin, the secondary tackifying  
6     resin or plasticizing oil, and stabilizer have been  
7     added, have been found to possess properties which  
8     are admirably suitable for the construction of  
9     disposable articles wherein the adhesive is applied  
10    as a continuous or discontinuous phase, or substrate,  
11    between members, e.g., via brushing, spraying or air-  
12    extrusion, between members to be bound together,  
13    articles, particularly disposable articles of multi-  
14    line construction wherein the adhesive is applied as  
15    fine parallel longitudinal strips, swirled, or as a  
16    multi-dot pattern of adhesive droplets, to bond  
17    together a moisture impervious outer polyethylene or  
18    polypropylene sheet and an inner moisture absorbent  
19    sheet, or tissue, as used in diaper constructions.  
20    These adhesive compositions have also been found  
21    suitable for use in the construction of sanitary  
22    napkins, bed pads, and, with or without the addition  
23    of other materials, are also useful for packaging and  
24    carton sealing, magazine and book lining, or book  
25    binding, or as elastic glues generally. These hot-  
26    melt adhesive compositions can be melted, and  
27    maintained under a blanketing nitrogen atmosphere, at  
28    relatively low to high temperatures without thermal  
29    degradation. The compositions can be applied in  
30    fluid form to polyethylene and polypropylene sub-  
31    strates as continuous or discontinuous films,  
32    suitably as fine lines or as patterns of multi-dots,  
33    without any risk of damage to the polyethylene or  
34    polypropylene substrate. These hot-melt adhesive  
35    compositions have also been found to serve a con-

1       struction function in binding together an outer  
2       sheet, or wrapper overlapped with an absorbent pad as  
3       required in the construction of sanitary napkins.  
4       The hot-melt adhesive composition applied as a fluid  
5       permeates the overlapped area to bind and seal the  
6       absorbent pad inside the outer sheet which serves as  
7       a wrapper.

8               The primary tackifying resins useful in the  
9       practice of this invention include hydrocarbon  
10       resins, synthetic polyterpenes, rosin esters and  
11       natural terpenes which are semi-solid or solid at  
12       ambient temperatures, and soften or become liquid at  
13       temperatures ranging generally from about 70°C to  
14       about 135°C, preferably from about 85°C to about  
15       120°C. Exemplary of the primary tackifying resins  
16       are compatible resins such as (1) natural and  
17       modified rosins such, for example, as gum rosin, wood  
18       rosin, tall oil rosin, distilled rosin, hydrogenated  
19       rosin, dimerized rosin, and polymerized rosin;  
20       (2) glycerol and pentaerythritol esters of natural  
21       and modified rosins, such, for example, as the  
22       glycerol ester of pale, wood rosin, the glycerol  
23       ester of hydrogenated rosin, the glycerol ester of  
24       polymerized rosin, the pentaerythritol ester of  
25       hydrogenated rosin, and the phenolic-modified  
26       pentaerythritol ester of rosin; (3) copolymers and  
27       terpolymers of natured terpenes, e.g., styrene/  
28       terpene and alpha methyl styrene/terpene; (4)  
29       polyterpene resins having a softening point, as  
30       determined by ASTM method E28-58T, of from about 80°  
31       to 150°C; the latter polyterpene resins generally  
32       resulting from the polymerization of terpene hydro-  
33       carbons, such as the bicyclic monoterpene known as  
34       pinene, in the presence of Friedel-Crafts catalysts  
35       at moderately low temperatures; also included are

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1 the hydrogenated polyterpene resins; (5) phenolic  
2 modified terpene resins and hydrogenated derivatives  
3 thereof such, for example, as the resin product  
4 resulting from the condensation, in an acidic medium,  
5 of a bicyclic terpene and a phenol; (6) aliphatic  
6 petroleum hydrocarbon resins having a Ball and Ring  
7 softening point of from about 70° to 135°C; the  
8 latter resins resulting from the polymerization of  
9 monomers consisting primarily of olefins and diole-  
10 fins; also included are the hydrogenated aliphatic  
11 petroleum hydrocarbon resins; (7) aromatic petroleum  
12 hydrocarbon resins, and mixed aromatic and aliphatic  
13 paraffin hydrocarbon resins, and the hydrogenated  
14 derivatives thereof; (8) aromatic modified alicyclic  
15 petroleum hydrocarbon resins and the hydrogenated  
16 derivatives thereof; and (9) alicyclic petroleum  
17 hydrocarbon resins and the hydrogenated derivatives  
18 thereof. The preferred primary tackifying resins for  
19 use in the practice of this invention are represented  
20 by sub-paragraphs (1), (3) and (7), supra. Suitable  
21 secondary tackifying resins are those named species  
22 wherein the resin is a liquid at ambient tempera-  
23 ture.

24 Various plasticizing oils are useful in the  
25 practice of this invention. The plasticizing oil can  
26 be used in place of or in combination with the  
27 secondary tackifier to reduce viscosity and improve  
28 tack properties. Plasticizing oils which have been  
29 found useful include olefin oligomers and low molecu-  
30 lar weight polymers as well as vegetable and animal  
31 oil and their derivatives. The petroleum derived  
32 oils which may be employed are relatively high  
33 boiling materials containing only a minor proportion  
34 of aromatic hydrocarbons (preferably less than 30%  
35 and, more particularly, less than 15% by weight of

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1 the oil). Alternately, the oil may be totally non-  
2 aromatic. The oligomers may be polypropylenes, poly-  
3 butenes, hydrogenated polyisoprene, hydrogenated  
4 polybutadiene, polypiperylene and copolymers of  
5 piperylene and isoprene, or the like having average  
6 molecular weights between about 350 and about  
7 10,000. Vegetable and animal oils include glyceryl  
8 esters of the usual fatty acids and polymerization  
9 products thereof.

10 The stabilizer, or antioxidant, used in  
11 accordance with the practice of this invention in-  
12 cludes high molecular weight hindered phenols and  
13 multifunctional phenols such as sulfur and phospho-  
14 rous-containing phenols. Hindered phenols are well  
15 known to those skilled in the art and may be charac-  
16 terized as phenolic compounds which also contain  
17 sterically bulky radicals in close proximity to the  
18 phenolic hydroxyl group thereof. In particular,  
19 tertiary butyl groups generally are substituted onto  
20 the benzene ring in at least one of the ortho posi-  
21 tions relative to the phenolic hydroxy group. The  
22 presence of these sterically bulky substituted radi-  
23 cals in the vicinity of the hydroxyl group serves to  
24 retard its stretching frequency and, correspondingly,  
25 its reactivity; this steric hindrance thus providing  
26 the phenolic compound with its stabilizing proper-  
27 ties. Representative hindered phenols include:  
28 1,3,5-trimethyl 2,4,6-tris (3,5-di-tert-butyl-4-  
29 hydroxybenzyl) benzene; pentaerythrityl tetrakis-3  
30 (3,5-di-tertbutyl-4-hydroxyphenyl) propionate;  
31 n-octadecyl-3,3,5-di-tert-butyl-4-hydroxyphenyl)-  
32 propionate; 4,4'-methylenbis (2,6-tert-butylphenol);  
33 4,4'-thiobis (6-tert-butyl-o-cresol); 2,6-di-tert-  
34 butylphenol; 6-(4-hydroxyphenoxy)-2,4-bis(n-octyl-  
35 thio)-1,3,5 triazine; di-n-octadecyl 3,5-di-tert-



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1 butyl-4-hydroxy-benzylphosphonate; 2-(n-octylthio)  
2 ethyl 3,5-di-tert-butyl-4-hydroxy-benzoate; and  
3 sorbitol [hex 3-(3,5-di-tert-butyl-4-hydroxyphenyl)-  
4 propionate.]

5 The hot-melt adhesive composition is pre-  
6 pared for use by blending the radial block copolymer  
7 with the primary tackifying resin, the secondary  
8 tackifying resin or plasticizing oil, and stabilizer,  
9 in any order or sequence, or these materials can be  
10 added together simultaneously to form the adhesive  
11 composition. In commercial practice it would be  
12 expected that the primary tackifying resin and  
13 copolymer, with or without the simultaneous addition  
14 of the secondary tackifying resin or plasticiz-  
15 ing oil, and stabilizer, would be blended together  
16 at sufficiently elevated temperature to form a fluid  
17 melt. For example, the copolymer can be blended with  
18 the solid compatible primary tackifying resin at  
19 temperatures ranging from about 130°C to about 200°C,  
20 preferably at from about 150°C to about 180°C, to  
21 form a fluid melt. The secondary liquid tackifying  
22 resin, or plasticizing oil, and stabilizer, can then  
23 be added to the melt. Alternatively, the fluid melt  
24 can be prepared with all components of the adhesive  
25 composition present ab initio.

26 The following non-limiting examples, and  
27 comparative demonstrations, bring out the more  
28 salient features of the invention. All parts are  
29 given in terms of weight units except as may other-  
30 wise be indicated.

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1     Examples

2             In conducting the following tests the com-  
3     position and properties of the neat radial, and  
4     linear block copolymers which were prepared for  
5     making the adhesive compositions were determined by  
6     techniques "a," "b" and "c". In evaluating the  
7     performance characteristics of the adhesive composi-  
8     tions produced from the radial, and linear block  
9     copolymers test procedures "d" through "f" were  
10    employed, to wit:

11            a.     Styrene content - of the experimental  
12    radial, and linear block copolymers was determined  
13    from the proton nmr spectra. Samples were dissolved  
14    in a mixture of deuterated tetrachloroethane/  
15    tetrachloroethylene, and analyzed on a Bruker 90 MHz  
16    spectrometer. Styrene content was calculated from  
17    the spectra by the method of V. D. Mochel, Rubber  
18    Chem. and Tech., 34 40, 1200 (1967).

19            b.     Molecular Weight - of the experimental  
20    radial, and linear block copolymers was determined by  
21    GPC, using the method described by J. R. Runyon, et  
22    al, J. Polym. Sci. 13, 2359 (1969).

23            c.     Melt Flow Rate (MFR) - of the experi-  
24    mental radial, and linear block copolymers was  
25    determined according to ASTM method D-1238-82, using  
26    condition "G" (200°C, 5 Kg weight).

27            d.     Adhesive Melt Viscosity (ASTM D-3236)  
28    - Melt viscosities were measured at a temperature of  
29    130°C, using a Brookfield Thermosel viscometer. Low  
30    adhesive viscosities are a necessity for processing  
31    in multi-line, spray, and fiberization equipment. In  
32    addition, the viscosity must be low at relatively low  
33    processing temperatures in order to avoid distortion  
34    of the polyolefin backing when hot adhesive is  
35    applied.

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1                   e.     Shear Adhesion Failure Temperature  
2     (SAFT) - is a measure of the ability of the bond to  
3     withstand an elevated temperature rising at 10°F/15  
4     min., under a constant force which pulls the bond in  
5     the shear mode. Bonds 1 inch by 1 inch were formed  
6     of adhesive, on a Mylar (polyester) backing, to a  
7     stainless steel panel, using a 4.5 lb. rubber  
8     roller. The panel was suspended vertically in an  
9     oven at 32°C, and allowed to come to equilibrium. A  
10    1 kg weight was suspended from the free end of the  
11    adhesive tape, and the temperature was raised at  
12    10°F/15 min. The temperature at which the tape and  
13    weight fell from the panel was recorded. SAFT was  
14    reported as the average of three such determina-  
15    tions. Adhesives possessing high failure tempera-  
16    tures are essential for the assembly of disposable  
17    articles, which are often subjected to very high  
18    temperatures during storage and shipping. In  
19    addition, these articles are used (worn) at body  
20    temperature.

21                   f.     Shear Holding Power (Static Time to  
22    Failure Bond Test) - The cohesive strength of the ad-  
23    hesives was determined according to the general pro-  
24    cedures outlined in PSTC-7 and ASTM D-3654. A 1  
25    inch by 0.5 inch bond was applied to a stainless  
26    steel panel with a 4.5 lb rubber roller. The plate  
27    was suspended vertically and allowed to equilibrate  
28    at 35°C. A 1 Kg weight was suspended from the free  
29    end of the tape. The time at which the tape and  
30    weight fell from the panel was recorded. The shear  
31    hold (in min) was reported as the average of four  
32    such determinations. Long failure times are desir-  
33    able, since they indicate strong bonds, which are  
34    essential in certain areas of the disposable con-

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1       structions, which are subjected to considerable  
2       stress during use. .

3               Examples 1-4, which immediately follow,  
4       describe the synthesis, and certain characteristics  
5       of the (pS-pI-pB)<sub>n</sub>X radial polymers of this inven-  
6       tion. Examples 5-7, on the other hand, describe the  
7       synthesis and certain characteristics of the  
8       (pS-pI)<sub>n</sub>X radial polymers of this invention. Demon-  
9       stration 9 is a linear pS-pI-pS linear block copoly-  
10      mer of the type described in Application Serial No.  
11      393.545, supra; the performance of which when made  
12      into an adhesive is substantially equivalent to that  
13      of the radial block copolymers of this invention.  
14      Demonstration 8 is a radial styrene-butadiene block  
15      copolymer which has a styrene content comparable to  
16      that of the copolymers of this invention, but an  
17      adhesive produced therefrom has a SAFT performance  
18      which is inferior to the radial polymers of this  
19      invention. Additionally, for comparative purposes,  
20      Demonstrations 10-12 represent polymers obtained from  
21      commercial sources, formulated into adhesive composi-  
22      tions, and tested. Demonstration 10 thus describes  
23      the performance characteristics of an adhesive com-  
24      position formed from a radial polystyrene-  
25      polybutadiene copolymer produced by Shell Chemical  
26      Company; Demonstration 11 an adhesive composition  
27      formulated from a linear multiblock polystyrene-  
28      polybutadiene copolymer produced by Firestone Tire  
29      and Rubber Company; and Demonstration 12 an adhesive  
30      composition formed from a linear polystyrene-polyiso-  
31      prene-polystyrene copolymer produced by Enichem  
32      Americas, Inc.

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1           The preparation of the block copolymers,  
2           and certain characteristics of the block copolymers,  
3           as employed in Examples 1 through 7 and Demonstra-  
4           tions 8 and 9 are given as follows:

5           Example 1 (5145-45)

6           To a 5-gallon, stirred reactor under a  
7           nitrogen atmosphere were added 12.6 kg of cyclohexane  
8           and 905 g of styrene. The temperature of the reactor  
9           was brought to 50°C and 147 g of a 0.28 M solution  
10          of sec-butyllithium in cyclohexane was added.  
11          Polymerization was allowed to continue for 50  
12          minutes. The reaction mixture was cooled to 50°C and  
13          1148 g of isoprene was added. The isoprene was  
14          allowed to polymerize for 32 minutes during which the  
15          reaction temperature reached a maximum of 68°C. At  
16          the end of the 32 minutes, 34 g of butadiene was  
17          added and it was allowed to polymerize for an  
18          additional 30 minutes. Then 14 g of  $\text{SiCl}_4$  was added  
19          slowly over the course of 11 minutes. The reaction  
20          was allowed to continue for another 15 minutes before  
21          an excess of isopropanol was added to the reaction  
22          mixture to quench any residual Li alkyl. A hindered  
23          phenol antioxidant was added to the polymer solution  
24          which was then devolatilized in a vacuum oven under  
25          nitrogen at 100°C for 3 hours.

26          Size exclusion chromatography of the  
27          resultant polymer showed two peaks, a high molecular  
28          weight peak which was the radial or star shaped  
29          polymer comprising 78% of the total polymer and a  
30          lower molecular weight peak, comprising 22% of the  
31          total polymer, which was the diblock building block  
32          before coupling the chain ends using  $\text{SiCl}_4$ . From  
33          gel-permeation chromatography, GPC, it was estimated  
34          that each arm of the radial polymer was composed of a  
35          polystyrene block of 18,000 molecular weight and

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1 22,800 molecular weight polydiene. The melt flow  
2 rate was 61.8. Ultimate tensile of the material was  
3 2763 psi.

4 Example 2 (5146-14)

5 To a 5-gallon, stirred reactor under a ni-  
6 trogen atmosphere were added 12.6 kg of cyclohexane  
7 and 718 g of styrene. The temperature of the reactor  
8 was brought to 50°C and 134.6 g of a 0.317 M solution  
9 of sec-butyllithium in cyclohexane was added. Poly-  
10 merization was allowed to continue for 60 minutes.  
11 The reaction mixture was cooled to 50°C and 1328 g of  
12 isoprene was added. The isoprene was allowed to  
13 polymerize for 25 minutes during which the reaction  
14 temperature reached a maximum of 77°C. At the end of  
15 the 25 minutes, 34 g of butadiene was added and it  
16 was allowed to polymerize for an additional 18  
17 minutes. Then 13 g of  $\text{SiCl}_4$  was added slowly over  
18 the course of 6 minutes. The reaction was allowed to  
19 continue for another 19 minutes before an excess of  
20 isopropanol was added to the reaction mixture to  
21 quench any residual Li alkyl. A hindered phenol  
22 antioxidant was added to the polymer solution which  
23 was then devolatilized in a vacuum oven under  
24 nitrogen at 100°C for 3 hours.

25 Size exclusion chromatography of the  
26 resultant polymer showed two peaks, a high molecular  
27 weight peak which was the radial or star shaped  
28 polymer comprising 86% of the total polymer and a  
29 lower molecular weight peak, comprising 14% of the  
30 total polymer, which was the diblock building block  
31 before coupling the materials using  $\text{SiCl}_4$ . From the  
32 GPC it was estimated that each arm of the radial  
33 polymer was composed of a polystyrene block of 16,560  
34 molecular weight and 30,620 molecular weight poly-  
35 diene. The melt flow rate was 18.7. Ultimate

1        tensile of the material was 4430 psi.

2        Example 3 (5146-13)

3                To a 5-gallon, stirred reactor under a ni-  
4        trogen atmosphere were added 12.6 kg of cyclohexane  
5        and 970 g of styrene. The temperature of the reactor  
6        was brought to 50°C and 139.0 g of a 0.317 M solution  
7        of sec-butyllithium in cyclohexane was added. Poly-  
8        merization was allowed to continue for 88 minutes.  
9        The reaction mixture was cooled to 50°C and 1086 g of  
10       isoprene was added. The isoprene was allowed to  
11       polymerize for 39 minutes during which the reaction  
12       temperature reached a maximum of 66°C. At the end of  
13       the 39 minutes, 34 g of butadiene was added and it  
14       was allowed to polymerize for an additional 33  
15       minutes. Then 13 g of  $\text{SiCl}_4$  was added slowly over  
16       the course of 8 minutes. The reaction was allowed to  
17       continue for another 18 minutes before an excess of  
18       isopropanol was added to the reaction mixture to  
19       quench any residual Li alkyl. A hindered phenol  
20       antioxidant was added to the polymer solution which  
21       was then devolatilized in a vacuum oven under  
22       nitrogen at 100°C for 3 hours.

23                Size exclusion chromatography of the  
24        resultant polymer showed two peaks, a high molecular  
25        weight peak which was the radial or star shaped  
26        polymer comprising 87% of the total polymer and a  
27        lower molecular weight peak, comprising 13% of the  
28        total polymer, which was the diblock building block  
29        before coupling the materials using  $\text{SiCl}_4$ . From the  
30        GPC it was estimated that each arm of the radial  
31        polymer was composed of a polystyrene block of 20,960  
32        molecular weight and 23,440 molecular weight poly-  
33        diene. The melt flow rate was 29.4. Ultimate  
34        tensile of the material was 3316 psi.

1     Example 4 (5146-16)

2             To a 5-gallon, stirred reactor under a ni-  
3     trogen atmosphere were added 12.6 kg of cyclohexane  
4     and 851 g of styrene. The temperature of the reactor  
5     was brought to 50°C and 121.8 g of 0.317 M solution  
6     of sec-butyllithium in cyclohexane was added.  
7     Polymerization was allowed to continue for 54  
8     minutes. The reaction mixture was cooled to 50°C and  
9     1200 g of isoprene was added. The isoprene was  
10    allowed to polymerize for 31 minutes during which the  
11    reaction temperature reached a maximum of 74°C. At  
12    the end of the 31 minutes, 34 g of butadiene was  
13    added and it was allowed to polymerize for an  
14    additional 20 minutes. Then 12 g of SiCl<sub>4</sub> was added  
15    slowly over the course of 6 minutes. The reaction  
16    was allowed to continue for another 16 minutes before  
17    an excess of isopropanol was added to the reaction  
18    mixture to quench any residual Li alkyl. A hindered  
19    phenol antioxidant was added to the polymer solution  
20    which was then devolatilized in a vacuum oven under  
21    nitrogen at 100°C for 3 hours.

22            Size exclusion chromatography of the  
23    resultant polymer showed two peaks, a high molecular  
24    weight peak which was the radial or star shaped  
25    polymer comprising 87% of the total polymer and a  
26    lower molecular weight peak, comprising 13% of the  
27    total polymer, which was the diblock building block  
28    before coupling the materials using SiCl<sub>4</sub>. From the  
29    GPC it was estimated that each arm of the radial  
30    polymer was composed of a polystyrene block of 20,730  
31    molecular weight and 29,200 molecular weight poly-  
32    diene. The 20 melt flow rate was 21.9. Ultimate  
33    tensile of the material was 3500 psi.



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1     Example 5 (5280-18)

2             To a 5-gallon, stirred reactor under a ni-  
3     trogen atmosphere were added 12.6 kg of cyclohexane  
4     and 901 g of styrene. The temperature of the reactor  
5     was brought to 50°C and 129.2 g of a 0.317 M solution  
6     of sec-butyllithium in cyclohexane was added. Poly-  
7     merization was allowed to continue for 55 minutes.  
8     The reaction mixture was cooled to 50°C and 1147.1 g  
9     of isoprene was added. The isoprene was allowed to  
10    polymerize for 31 minutes during which the reaction  
11    temperature reached a maximum of 69°C. At the end of  
12    the 31 minutes, 23.7 g of  $\text{SiCl}_4$  was added slowly over  
13    the course of 6 minutes. The reaction was allowed to  
14    continue for another 30 minutes before an excess of  
15    isopropanol was added to the reaction mixture to  
16    quench any residual Li alkyl. A hindered phenol  
17    antioxidant was added to the polymer solution which  
18    was then devolatilized in a vacuum oven under  
19    nitrogen at 100°C for 3 hours.

20            Size exclusion chromatography of the  
21    resultant polymer showed two peaks, a high molecular  
22    weight peak which was the radial or star shaped  
23    polymer comprising 82.2% of the total polymer and a  
24    lower molecular weight peak, comprising 17.8% of the  
25    total polymer, which was the diblock building block  
26    before coupling the materials using  $\text{SiCl}_4$ . From the  
27    GPC it was estimated that each arm of the radial  
28    polymer was composed of a polystyrene block of 21,021  
29    molecular weight and 26,755 molecular weight polyiso-  
30    prene. The melt flow rate was 8.1 g/10 minutes.  
31    Ultimate tensile of the material was 3620 psi.

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1     Example 6 (5280-19)

2             To a 5-gallon, stirred reactor under a ni-  
3     trogen atmosphere were added 12.6 kg of cyclohexane  
4     and 714.8 g of styrene. The temperature of the reac-  
5     tor was brought to 50°C and 111.7 g of a 0.317 M  
6     solution of sec-butyllithium in cyclohexane was  
7     added. Polymerization was allowed to continue for 53  
8     minutes. The reaction mixture was cooled to 50°C and  
9     1327.4 g of isoprene was added. The isoprene was  
10    allowed to polymerize for 41 minutes during which the  
11    reaction temperature reached a maximum of 74°C. At  
12    the end of the 41 minutes, 20.5 g of SiCl<sub>4</sub> was added  
13    slowly over the course of 6 minutes. The reaction  
14    was allowed to continue for another 30 minutes before  
15    an excess of isopropanol was added to the reaction  
16    mixture to quench any residual Li alkyl. A hindered  
17    phenol antioxidant was added to the polymer solution  
18    which was then devolatilized in a vacuum oven under  
19    nitrogen at 100°C for 3 hours.

20            Size exclusion chromatography of the  
21    resultant polymer showed two peaks, a high molecular  
22    weight peak which was the radial or star shaped  
23    polymer comprising 78.7% of the total polymer and a  
24    lower molecular weight peak, comprising 21.3% of the  
25    total polymer, which was the diblock building block  
26    before coupling the materials using SiCl<sub>4</sub>. From the  
27    GPC it was estimated that each arm of the radial  
28    polymer was composed of a polystyrene block of 19,138  
29    molecular weight and 35,541 molecular weight polyiso-  
30    prene. The melt flow rate was 5.7 g/10 minutes.  
31    Ultimate tensile of the material was 4210 psi.

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1     Example 7 (5280-20)

2             To a 5-gallon, stirred reactor under a ni-  
3     trogen atmosphere were added 12.6 kg of cyclohexane  
4     and 964.2 g of styrene. The temperature of the  
5     reactor was brought to 50°C and 118.5 g of a 0.317 M  
6     solution of sec-butyllithium in cyclohexane was  
7     added. Polymerization was allowed to continue for 53  
8     minutes. The reaction mixture was cooled to 50°C and  
9     1087.3 g of isoprene was added. The isoprene was  
10    allowed to polymerize for 35 minutes during which the  
11    reaction temperature reached a maximum of 69°C. At  
12    the end of the 35 minutes, 21.8 g of SiCl<sub>4</sub> was added  
13    slowly over the course of 6 minutes. The reaction  
14    was allowed to continue for another 32 minutes before  
15    an excess of isopropanol was added to the reaction  
16    mixture to quench any residual Li alkyl. A hindered  
17    phenol antioxidant was added to the polymer solution  
18    which was then devolatilized in a vacuum oven under  
19    nitrogen at 100°C for 3 hours.

20            Size exclusion chromatography of the  
21    resultant polymer showed two peaks, a high molecular  
22    weight peak which was the radial or star shaped  
23    polymer comprising 84.8% of the total polymer and a  
24    lower molecular weight peak, comprising 15.2% of the  
25    total polymer, which was the diblock building block  
26    before coupling the materials using SiCl<sub>4</sub>. From the  
27    GPC it was estimated that each arm of the radial  
28    polymer was composed of a polystyrene block of 24,534  
29    molecular weight and 27,666 molecular weight polyiso-  
30    prene. The melt flow rate was 8.9 g/10 minutes.  
31    Ultimate tensile of the material was 3340 psi.

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1        Demonstration 8 (5145-49)

2                To a 5-gallon, stirred reactor under a ni-  
3        trogen atmosphere were added 12.5 kg of cyclohexane  
4        and 911.6 g of styrene. The temperature of the  
5        reactor was brought to 50°C and 170.8 g of a 0.317 M  
6        solution of sec-butyllithium in cyclohexane was  
7        added. Polymerization was allowed to continue for 46  
8        minutes. The reaction mixture was cooled to 50°C and  
9        1123 g of butadiene was added. The butadiene was  
10       allowed to polymerize for 46 minutes during which the  
11       reaction temperature reached a maximum of 69°C. At  
12       the end of the 46 minutes, 21.5 g of SiCl<sub>4</sub> was added  
13       slowly over the course of 10 minutes. The reaction  
14       was allowed to continue for another 17 minutes before  
15       an excess of isopropanol was added to the reaction  
16       mixture to quench any residual Li alkyl. A hindered  
17       phenol antioxidant was added to the polymer solution  
18       which was then devolatilized in a vacuum oven under  
19       nitrogen at 100°C for 3 hours.

20               Size exclusion chromatography of the  
21       resultant polymer showed two peaks, a high molecular  
22       weight peak which was the radial or star shaped  
23       polymer comprising 76.3% of the total polymer and a  
24       lower molecular weight peak, comprising 23.7% of the  
25       total polymer, which was the diblock building block  
26       before coupling the materials using SiCl<sub>4</sub>. From the  
27       GPC it was estimated that each arm of the radial  
28       polymer was composed of a polystyrene block of 15,635  
29       molecular weight and 19,264 molecular weight polybut-  
30       adiene. The melt flow rate was 28.8 g/10 minutes.

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1     Demonstration 9 (5054-30)

2             To a 2.6 liter reactor were charged 1499 g  
3     of cyclohexane and 85.8 g of styrene monomer. The  
4     mixture was heated to 60°C and 7.8 ml of a 0.70 molar  
5     solution of sec-butyllithium initiator in cyclohexane  
6     was added. After 41 minutes, the reaction tempera-  
7     ture was reduced to 58°C and 118.5 grams of isoprene  
8     was added. After 39 minutes the living styrene-  
9     isoprene diblock polymer was coupled to form a linear  
10    styrene-isoprene-styrene triblock polymer by adding  
11    32 ml of 0.12 M 1,2-dibromoethane in cyclohexane over  
12    a period of 11 minutes. A hindered phenol antioxi-  
13    dant was added to the polymer solution which was then  
14    devolatized in a vacuum oven under nitrogen at 100°C  
15    for 3 hours.

16            Size exclusion chromatography of the resul-  
17    tant polymer showed two peaks, a high molecular  
18    weight peak which was the linear triblock polymer  
19    comprising 86.5% of the total polymer and a lower  
20    molecular weight peak, comprising 13.5% of the total  
21    polymer, which was the diblock building block before  
22    coupling the chain ends using DBE. From the GPC it  
23    was estimated that the molecular weight of the  
24    styrene blocks was 16,660, and the molecular of the  
25    polyisoprene midblock was 42,580. The melt flow rate  
26    was 50 g/10 minutes.

27            Adhesive compositions were prepared by com-  
28    bining 100 parts of the block copolymer, 220 parts of  
29    the primary tackifying resin (Zonatac 105L, available  
30    from Arizona Chemical), 80 parts of Tufflo 6056  
31    (a plasticizer oil available from Lyondell Petroleum  
32    Company), and 3 parts of Irganox 1010 (a stabilizer  
33    available from Ciba-Geigy), to produce a homogeneous  
34    adhesive blend. The adhesive was coated on 2 mil

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1 thick Mylar (polyester) backing, to produce a 1.5 mil  
2 thick film, of adhesive.

3           The performance characteristics of the ad-  
4 hesives of the block copolymers are given in the  
5 Table, the adhesive formulations for the  
6 (pS-pI-pB)<sub>n</sub>X and (pS-pI)<sub>n</sub>X radial block copolymers,  
7 or "rubbers" of this invention, designated as  
8 Examples 1 through 7, being set out for comparison  
9 with adhesive formulations prepared from rubbers not  
10 of this invention, i.e., Demonstrations 8-12.  
11 Columns 1 and 2 of the Table identifies the specific  
12 test run and type of rubber tested. Columns 3-6  
13 identifies the MFR, or Melt Flow Rate, the total wt.%  
14 styrene content of the rubber, the molecular weight  
15 of the polystyrene block component of a rubber, pS,  
16 and the molecular weight of the polyisoprene block  
17 component of a rubber, pI. Columns 7-9 describe the  
18 results of the tests conducted on each of the  
19 adhesive formulations, viz. the adhesive viscosity,  
20 SAFT, and the holding power. It is clear that the  
21 adhesive compositions of this invention, i.e.,  
22 Examples 1-7, exhibit superior SAFT (high temperature  
23 resistance), and superior holding power (static time  
24 to failure).

ADHESIVE FORMULATION:

Table

| RUBBER                           | TYPE          | MFR  | WT %<br>STYRENE | POLYSTYRENE |        | POLYDIENE (pD) |        | ADHES.<br>VISC.<br>130 C<br>(CPS) | SAFT<br>(C) | 35 C<br>HOLD<br>(MIN) |
|----------------------------------|---------------|------|-----------------|-------------|--------|----------------|--------|-----------------------------------|-------------|-----------------------|
|                                  |               |      |                 | MOL WT      | MOL WT | MOL WT         | MOL WT |                                   |             |                       |
| Block Copolymer (RUBBER)         |               |      |                 |             |        |                |        |                                   |             |                       |
| Primary Tackifier (ZONATAC 105L) |               |      |                 |             |        |                |        |                                   |             |                       |
| Plasticizer Oil (TUFFLO 6056)    |               |      |                 |             |        |                |        |                                   |             |                       |
| Stabilizer (IRGANOX 1010)        |               |      |                 |             |        |                |        |                                   |             |                       |
| PHR                              |               |      |                 |             |        |                |        |                                   |             |                       |
| 100                              |               |      |                 |             |        |                |        |                                   |             |                       |
| 220                              |               |      |                 |             |        |                |        |                                   |             |                       |
| 80                               |               |      |                 |             |        |                |        |                                   |             |                       |
| 3                                |               |      |                 |             |        |                |        |                                   |             |                       |
| EXAMPLE 1                        | (pS-pI-pB)n-X | 61.8 | 44.1            | 18006       | 22823  | 7538           | 83.6   | >4000                             |             |                       |
| EXAMPLE 2                        | (pS-pI-pB)n-X | 18.7 | 35.1            | 16561       | 30621  | 7425           | 80.4   | >4000                             |             |                       |
| EXAMPLE 3                        | (pS-pI-pB)n-X | 29.4 | 47.2            | 20955       | 23441  | 17425          | 88.7   | >4000                             |             |                       |
| EXAMPLE 4                        | (pS-pI-pB)n-X | 40.3 | 41.5            | 20726       | 29216  | 13325          | 88.1   | >4000                             |             |                       |
| EXAMPLE 5                        | (pS-pI)n-X    | 8.1  | 45.3            | 21021       | 26755  | 14425          | 84.4   | >4000                             |             |                       |
| EXAMPLE 6                        | (pS-pI)n-X    | 5.7  | 35.3            | 19138       | 35541  | 18700          | 80.9   | >4000                             |             |                       |
| EXAMPLE 7                        | (pS-pI)n-X    | 8.9  | 47.1            | 24534       | 27666  | 17500          | 88.6   | >4000                             |             |                       |
| DEMONSTRATION 8                  | (pS-pB)n-X    | 28.8 | 44.8            | 15635       | 19264  | 9050           | 76.8   | >4000                             |             |                       |
| DEMONSTRATION 9                  | pS-pI-pS      | 50   | 43.9            | 16660       | 42580  | 8875           | 83.2   | >4000                             |             |                       |
| DEMONSTRATION 10                 | (pS-pB)n-X    | 3.3  | 39.7            | 14211       | 21585  | 15350          | 72.6   | >4000                             |             |                       |
| (KRATON D1122)                   |               |      |                 |             |        |                |        |                                   |             |                       |
| DEMONSTRATION 11                 | (pS-pB)n-pS   | 12.4 | 42.3            |             |        | 9575           | 68.3   | 453                               |             |                       |
| (STEREON 840A)                   |               |      |                 |             |        |                |        |                                   |             |                       |
| DEMONSTRATION 12                 | pS-pI-pS      | 12.8 | 24.2            | 13189       | 82622  | 7650           | 68.7   | 395                               |             |                       |
| (EUROPENE SOLT193B)              |               |      |                 |             |        |                |        |                                   |             |                       |

## LEGEND:

pS = POLYSTYRENE BLOCK  
 pI = POLYISOPRENE BLOCK  
 pB = POLYBUTADIENE BLOCK  
 pD = POLYDIENE BLOCK = (pI+pB)

## NOTES:

- (1) KRATON is a trademark of Shell Chemical Company
- (2) STERON is a trademark of Firestone Tire and Rubber Company
- (3) EUROPENE is a trademark of Enichem Americas, Inc.

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Continuing reference to the Table, Examples 1 through 7 show the performance of adhesive compositions prepared from radial block polymers whose % styrene, polystyrene molecular weight, and polydiene molecular weight are all within the preferred ranges of the radial block copolymer required for the practice of this invention. It is required that all of these parameters fall within the ranges expressed in order to obtain this superior adhesive performance. Comparative Example 8, showing the performance characteristics of an adhesive composition of a radial styrene-butadiene copolymer not of this invention, albeit the copolymer has a styrene content and melt flow rate comparable to the radial copolymers of this invention, is inadequate. Its shear adhesion failure temperature, SAFT, is very poor. Styrene-isoprene copolymers have inherently lower viscosity than styrene-butadiene copolymers of the same molecular weight, and hence the styrene-isoprene copolymers are superior in that they can be made with higher molecular weight pS blocks. As a result, the styrene-isoprene copolymers can be produced with greater SAFT. Comparative Example 9 shows the performance characteristics of an adhesive composition made from a linear pS-pI-pS copolymer as disclosed in Application Ser. No. 393,545, supra. Demonstrations 10, 11 and 12 represent adhesive compositions prepared from commercially available copolymers having properties which fall outside those requirements which are necessary to obtain superior hot-melt adhesives, i.e., a radial (pS-pB)<sub>n</sub>X block copolymer as represented by Demonstrations 10 (Kraton D 1122), a (pS-pB)<sub>n</sub> pS linear multiblock copolymer as represented by Demonstration 11 (Stereon 34 840A), and a linear pS-pI-pS block copolymer as represented by



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1        Demonstration 12 (Europrene SOL T 193 B). As shown  
2        by the Table, the adhesive compositions of Examples 1  
3        through 7 clearly exhibit the best combination of low  
4        adhesive viscosity, high SAFT, and high 35°C Hold.

5                A prepared adhesive composition useful for  
6        magazine or book binding can also be formed from the  
7        hot-melt adhesive composition of this invention by  
8        the further addition to the hot-melt adhesive compo-  
9        sition of from 0 to about 5 percent, preferably from  
10       about 0.5 to about 5 percent, based on the weight of  
11       the hot-melt adhesive composition, of a hydrocarbon  
12       or petroleum derived wax. Exemplary petroleum  
13       derived waxes are, e.g., paraffin and microcrystal-  
14       line waxes having melting points within a range of  
15       from about 55°C to about 110°C, as well as low  
16       molecular weight polyethylene and Fischer-Tropsch  
17       waxes.

18               It is apparent that various modifications and  
19       changes can be made without departing the spirit and  
20       scope of the invention.

21               Having described the invention, what is claimed  
22       is:

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1           1.    A composition of matter useful in forming  
2   hot-melt adhesives which comprises

3                a radial block copolymer constituted of a  
4   polystyrene block segment and a polyisoprene block  
5   segment, or polyisoprene block segment an end of  
6   which is constituted of butadiene, as characterized  
7   by either of the formulas:

8                (1)   (pS-pI)<sub>n</sub>X, or

9                (2)   (pS-pI-pB)<sub>n</sub>X

10   where pS is polystyrene, pI is polyisoprene, pB is  
11   polybutadiene, X is the residue of a multifunctional  
12   coupling agent used in the production of the radial  
13   block copolymer, and n is a number greater than 2  
14   representative of the number of branches appended to  
15   X,

16                pS has an average number molecular weight  
17   ranging from about 10,000 to about 25,000, pI has an  
18   average number molecular weight ranging from about  
19   20,000 to about 70,000, (pI-pB) has an average number  
20   molecular weight ranging from about 20,000 to about  
21   70,000, the overall number average molecular weight  
22   of the block copolymer ranges from about 90,000 to  
23   about 380,000, and wherein the pS component is  
24   present in an amount of at least 25 parts to about 50  
25   parts per 100 parts by weight of the radial block  
26   copolymer.

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1           2.    The composition of Claim 1 wherein the  
2    average molecular weight of the pI or (pI+pB) compo-  
3    nents of the radial block copolymer ranges from about  
4    20,000 to about 40,000, the average molecular weight  
5    of the pS component ranges from about 14,000 to about  
6    20,000, the overall molecular weight of the copolymer  
7    ranges from about 100,000 to about 240,000, and  
8    wherein the pS component is present in amount ranging  
9    from about 27 parts to about 45 parts per 100 parts  
10   by weight of the copolymer.

1           3.    A hot melt adhesive composition useful in  
2    the assembly of disposable articles which comprises  
3                from about 15 percent to about 35 percent  
4    based on the weight of the hot-melt adhesive composi-  
5    tion, of a radial block copolymer constituted of a  
6    polystyrene block segment and a polyisoprene block  
7    segment, or polyisoprene block segment an end of  
8    which is constituted of butadiene, as characterized  
9    by either of the formulas:

8               (1)   (pS-pI)<sub>n</sub>X, or

9               (2)   (pS-pI-pB)<sub>n</sub>X

10   where pS is polystyrene, pI is polyisoprene, pB is  
11   polybutadiene, X is the residue of a multifunctional  
12   coupling agent used in the production of the radial  
13   block copolymer, and n is a number greater than 2  
14   representative of the number of branches appended to  
15   X.

16               pS has an average number molecular weight  
17   ranging from about 10,000 to about 25,000, pI has an  
18   average number molecular weight ranging from about  
19   20,000 to about 70,000, (pI+pB) has an average number  
20   molecular weight ranging from about 20,000 to about

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21 70,000, the overall number average molecular weight  
22 of the block copolymer ranges from about 90,000 to  
23 about 380,000, and wherein the pS component is  
24 present in an amount of at least 25 parts to about 50  
25 parts per 100 parts by weight of the radial block  
26 copolymer

27 from about 45 percent to about 70 percent  
28 of a compatible primary tackifying resin, based on  
29 the weight of the hot-melt adhesive composition,

30 from 0 percent to about 30 percent of a  
31 plastizing oil or secondary tackifying resin, based  
32 on the weight of the hot melt adhesive composition,  
33 and

34 from about 0.1 percent to about 2 percent  
35 of a stabilizer, based on the weight of the hot-melt  
36 adhesive composition.

1 4. The composition of Claim 3 wherein the hot  
2 melt adhesive composition contains from about 20  
3 percent to about 30 percent of the copolymer.

1 5. The composition of Claim 3 wherein the hot  
2 melt adhesive composition contains from about 50  
3 percent to about 60 percent of the compatible primary  
4 tackifying resin.

1 6. The composition of Claim 3 wherein the hot-  
2 melt adhesive composition contains from about 5  
3 percent to about 20 percent of the plasticizing oil  
4 or secondary tackifying resin.

1 7. The composition of Claim 3 wherein the hot-  
2 melt adhesive composition contains from about 0.5  
3 percent to about 1.5 percent of the stabilizer.

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1           8.    The composition of Claim 3 wherein the  
2           average molecular weight of the pI or (pI+pB) compo-  
3           nents of the radial block copolymer ranges from about  
4           20,000 to about 40,000, the average molecular weight  
5           of the pS component ranges from about 14,000 to about  
6           20,000, the overall molecular weight of the copolymer  
7           ranges from about 100,000 to about 240,000, and  
8           wherein the pS component is present in amount ranging  
9           from about 27 parts to about 45 parts per 100 parts  
10          by weight of the copolymer.

1           9.    The composition of Claim 3 wherein the hot-  
2           melt adhesive composition additionally contains up  
3           to about 5 percent, based on the weight of the  
4           hot-melt adhesive composition, of a hydrocarbon wax  
5           sufficient to form an adhesive composition useful for  
6           lining magazines or books, or for packaging and  
7           carton sealing.

1           10.   A disposable article comprising a polyethy-  
2           lene or polypropylene substrate bonded to a tissue,  
3           non-woven, polyethylene or polypropylene, substrate  
4           using a hot-melt adhesive composition which comprises  
5           from about 15 percent to about 35 percent,  
6           based on the weight of the hot-melt adhesive composi-  
7           tions, of a radial block copolymer constituted of a  
4           polystyrene block segment and a polyisoprene block  
5           segment, or polyisoprene block an end of which is  
6           constituted of butadiene, as characterized by either  
7           of the formulas:

- 8                   (1)   (pS-pI)<sub>n</sub>X, or  
9                   (2)   (pS-pI-pB)<sub>n</sub>X

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10 where pS is polystyrene, pI is polyisoprene, pB is  
11 polybutadiene, X is the residue of a multifunctional  
12 coupling agent used in the production of the radial  
13 block copolymer, and n is a number greater than 2  
14 representative of the number of branches appended to  
15 X,

16 pS has an average number molecular weight  
17 ranging from about 10,000 to about 25,000, pI has an  
18 average number molecular weight ranging from about  
19 20,000 to about 70,000, (pI-pB) has an average number  
20 molecular weight ranging from about 20,000 to about  
21 70,000, the overall number average molecular weight  
22 of the block copolymer ranges from about 90,000 to  
23 about 380,000, and wherein the pS component is  
24 present in an amount of at least 25 parts to about 50  
25 parts per 100 parts by weight of the radial block  
26 copolymer,

27 from about 45 percent to about 70 percent  
28 of a compatible primary tackifying resin, based on  
29 the weight of the hot-melt adhesive composition,

30 from 0 percent to about 30 percent of a  
31 plastizing oil or secondary tackifying resin, based  
32 on the weight of the hot melt adhesive composition,  
33 and

34 from about 0.1 percent to about 2 percent  
35 of a stabilizer, based on the weight of the hot melt  
36 adhesive composition.

1 11. The article of manufacture according to  
2 Claim 10 wherein the hot-melt adhesive composition  
3 contains from about 20 percent to about 30 percent  
4 of the radial block copolymer.

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1           12.    The article of manufacture according to  
2           Claim 10 wherein the hot-melt adhesive composition  
3           contains from about 50 percent to about 60 percent  
4           of the compatible primary tackifying resin.

1           13.    The article of manufacture according to  
2           Claim 10 wherein the hot melt adhesive composition  
3           contains from about 5 percent to about 20 percent  
4           of the plasticizing oil or secondary tackifying  
5           resin.

1           14.    The article of manufacture according to  
2           Claim 10 wherein the hot melt adhesive composition  
3           contains from about 0.5 percent to about 1.5 percent  
4           of the stabilizer.

1           15.    The article of manufacture according to  
2           Claim 10 wherein the average molecular weight of  
3           the pI or (pI+pB) components of the radial block  
4           copolymer ranges from about 20,000 to about 40,000,  
5           the average molecular weight of a pS component ranges  
6           from about 14,000 to about 20,000, the overall  
7           molecular weight of the copolymer ranges from about  
8           100,000 to about 240,000, and wherein the pS compo-  
9           nent is present in amount ranging from about 27 parts  
10          to about 45 parts per 100 parts by weight of the  
11          copolymer.

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1           16.    The article of manufacture according to  
2           Claim 10 wherein the primary tackifying resin is any  
3           compatible resin or mixture thereof selected from the  
4           group consisting of (1) natural and modified rosins;  
5           (2) glycerol and pentaerythritol esters of natural  
6           and modified rosins; (3) copolymers and terpolymers  
7           of natured terpenes; (4) polyterpene resins having a  
8           softening point, as determined by ASTM method  
9           E28-58T, of from about 80° to 150°C; (5) phenolic  
10          modified terpene resins and hydrogenated derivatives  
11          thereof; (6) aliphatic petroleum hydrocarbon resins  
12          having a Ball and Ring softening point of from about  
13          70° to 135°C; (7) aromatic petroleum hydrocarbon  
14          resins, and mixed aromatic and aliphatic paraffin  
15          hydrocarbon resins, and the hydrogenated derivatives  
16          thereof; (8) aromatic modified alicyclic petroleum  
17          hydrocarbon resins and the hydrogenated derivatives  
18          thereof; and (9) alicyclic petroleum hydrocarbon  
19          resins and the hydrogenated derivatives thereof.

1           17.    The article of manufacture according to  
2           Claim 10 wherein the disposable article is selected  
3           from the group consisting of diapers, sanitary  
4           napkins and bed pads.

1           18.    The article of manufacture according to  
2           Claim 10 wherein the adhesive component of the disposable  
3           article is applied as a discontinuous phase.

1           19.    The article of manufacture according to  
2           Claim 10 wherein the disposable article is of  
3           multi-line construction.



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1           20. The article of manufacture according to  
2           Claim 19 wherein the adhesive component used in  
3           forming the disposable article is applied as fine  
4           parallel longitudinal strips, swirl or as a multi-  
5           dot pattern of adhesive droplets.

## INTERNATIONAL SEARCH REPORT

PCT/US 92/04334

International Application No

|   |   |                                     |
|---|---|-------------------------------------|
| <b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>   |   |                                     |
| According to International Patent Classification (IPC) or to both National Classification and IPC   |   |                                     |
| Int.Cl. 5 C08F297/04; C08G81/02; C09J153/02; C09J7/02   |   |                                     |
| <b>II. FIELDS SEARCHED</b>  |   |                                     |
| Minimum Documentation Searched <sup>7</sup>   |   |                                     |
| Classification System   | Classification Symbols  |                                     |
| Int.Cl. 5   | C08F ; C08G ; C09J  |                                     |
| Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>  |   |                                     |
| <b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>   |   |                                     |
| Category <sup>10</sup>  | Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>  | Relevant to Claim No. <sup>13</sup> |
| X   | WORLD PATENTS INDEX LATEST<br>Week 8327,<br>Derwent Publications Ltd., London, GB;<br>AN 83-702656<br>& JP,A,58 089 672 (JAPAN SYNTHETIC RUBBER) 28<br>May 1983 | 1-9                                 |
| Y   | see abstract  | 1-20                                |
| Y   | EP,A,0 306 232 (MINNESOTA MINING AND<br>MANUFACTURING COMP.) 8 March 1989<br>see page 5, line 25 - line 29; claims  | 1-20                                |
| X   | US,A,4 096 203 (ST. CLAIR) 20 June 1978<br>see column 4, line 25 - line 44; claims 1-4  | 1-9                                 |
| -/--  |   |                                     |
| <p><sup>10</sup> Special categories of cited documents : <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> |   |                                     |
| <b>IV. CERTIFICATION</b>  |   |                                     |
| Date of the Actual Completion of the International Search   | Date of Mailing of this International Search Report   |                                     |
| 31 AUGUST 1992  | 11. 09. 92  |                                     |
| International Searching Authority   | Signature of Authorized Officer   |                                     |
| EUROPEAN PATENT OFFICE  | LOISELET-TAISNE S.  |                                     |

| III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET) |  |                       |
|--|--|-----------------------|
| Category °   | Citation of Document, with indication, where appropriate, of the relevant passages   | Relevant to Claim No. |
| X  | WORLD PATENTS INDEX LATEST<br>Week 8329,<br>Derwent Publications Ltd., London, GB;<br>AN 83-715139<br>& SU,A,956 532 (TRISHIN) 7 September 1982<br>see abstract<br>--- | 1-2                   |
| X  | EP,A,0 362 850 (KURARAY CO.) 11 April 1990<br>see block copolymer (E) shown in Table 2<br>see claims 4,6; table 2<br>---   | 1                     |
| P,A  | US,A,5 028 646 (MILLER ET AL.) 2 July 1991<br>see column 6, line 30 - line 31; examples<br>see column 6, line 38 - line 53; claims<br>---                              | 1,3-20                |
| A  | US,A,4 163 077 (ANTONSEN ET AL.) 31 July 1979<br>see claim 1<br>---  | 1,10                  |

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9204334  
SA 60795

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 31/08/92

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) |          | Publication<br>date |
|---|---------------------|----------------------------|----------|---------------------|
| EP-A-0306232                              | 08-03-89            | AU-A-                      | 2117188  | 02-03-89            |
|   |                     | JP-A-                      | 1095175  | 13-04-89            |
|   |                     | US-A-                      | 5112889  | 12-05-92            |
| -----                                     |                     |                            |          |                     |
| US-A-4096203                              | 20-06-78            | None                       |          |                     |
| -----                                     |                     |                            |          |                     |
| EP-A-0362850                              | 11-04-90            | JP-A-                      | 2300218  | 12-12-90            |
|   |                     | JP-A-                      | 2102212  | 13-04-90            |
|   |                     | JP-A-                      | 2135256  | 24-05-90            |
|   |                     | US-A-                      | 4987194  | 22-01-91            |
| -----                                     |                     |                            |          |                     |
| US-A-5028646                              | 02-07-91            | US-A-                      | 5112889  | 12-05-92            |
| -----                                     |                     |                            |          |                     |
| US-A-4163077                              | 31-07-79            | AU-B-                      | 520187   | 21-01-82            |
|   |                     | AU-A-                      | 4609879  | 25-10-79            |
|   |                     | CA-A-                      | 1134212  | 26-10-82            |
|   |                     | DE-A, C                    | 2916054  | 31-10-79            |
|   |                     | FR-A, B                    | 2423524  | 16-11-79            |
|   |                     | GB-A, B                    | 2019416  | 31-10-79            |
|   |                     | JP-C-                      | 1398694  | 07-09-87            |
|   |                     | JP-A-                      | 54145740 | 14-11-79            |
|   |                     | JP-B-                      | 62006597 | 12-02-87            |
|   |                     | NL-A-                      | 7902904  | 23-10-79            |
|   |                     | SE-B-                      | 446272   | 25-08-86            |
|   |                     | SE-A-                      | 7903273  | 18-10-79            |
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